To appear in *The Astrophysical Journal Letters*, the 2003-December-20th issue

On Titanium Carbide Nanoparticles as the Origin of the 21 Micron Emission Feature in Post-Asymptotic Giant Branch Stars

Aigen Li

Theoretical Astrophysics Program, Lunar and Planetary Laboratory and Steward Observatory, University of Arizona, Tucson, AZ 85721;
agli@lpl.arizona.edu

arXiv:astro-ph/0311068v1 4 Nov 2003

ABSTRACT

Titanium carbide (TiC) nanocrystals were recently proposed as the carrier of the mysterious 21 μm emission feature observed in post-asymptotic giant branch stars, based on their close spectral match and the presolar nature of meteoritic TiC nanograins (which reveals their stellar ejecta origin). But we show in this *Letter* that the Kramers-Kronig dispersion relations, which relate the wavelength-integrated extinction cross section to the total dust mass, would impose a lower bound on the TiC mass. This Kramers-Kronig lower limit exceeds the maximum available TiC mass by a factor of at least ~ 50, independent of the absolute value of the ultraviolet/visible absorptivity of nano TiC. The TiC model is therefore readily ruled out by the Kramers-Kronig physical principle.

Subject headings: circumstellar matter — dust, extinction — infrared: stars — stars: AGB and Post-AGB — stars: individual (HD 56126)

1. Introduction

A prominent broad (with a FWHM of $\sim 2\,\mu$m) emission feature at about $21\,\mu$m[1] was discovered by Kwok, Volk, & Hrivnak (1989) in an analysis of the *Infrared Astronomical Satellite* (IRAS) *Low Resolution Spectrometer* (LRS) spectra of four carbon-rich post-asymptotic giant branch (AGB) stars, and subsequently confirmed by both ground-based and airborne *Kuiper Airborne Observatory* and ISO observations (see Kwok, Volk, & Hrivnak 1999 and references therein). So far, this feature has been detected in twelve post-AGB stars (commonly termed as the "$21\,\mu$m sources"; Kwok et al. 1999)[2], with little shape variation found between different sources. These stars have quite uniform

[1] High resolution spectra obtained with the *Short-Wavelength Spectrometer* (SWS) instrument (with a resolution of $\lambda/\Delta\lambda \approx 2000$) on board the *Infrared Space Observatory* show that this feature actually peaks at $\sim 20.1\,\mu$m (Volk, Kwok, & Hrivnak 1999). But for historical reasons, this feature continues to be referred to as the "$21\,\mu$m feature".

[2] A weak $21\,\mu$m feature was recently reported for three planetary nebulae (PNs; Hony, Waters, & Tielens 2001; K. Volk 2003, in preparation).

properties: they are mostly metal-poor carbon-rich F and G supergiants with strong infrared (IR) excesses and overabundant s-process elements (see Kwok et al. 1999).

The carrier of this mysterious $21\,\mu$m feature remains unidentified, although many candidate materials have been proposed including iron oxides Fe_2O_3 or Fe_3O_4, hydrogenated amorphous carbon, hydrogenated fullerenes, hydrogenated nanodiamond, amides (thiourea or urea $OC\,[NH_2]_2$), SiS_2, oxygen-bearing side groups in coal (see Kwok et al. 1999 and references therein), and more recently titanium carbide (TiC) nanoclusters (von Helden et al. 2000), SiC (Speck & Hofmeister 2003), and stochastically-heated silicon core-SiO_2 mantle nanograins (Smith & Witt 2002; Li & Draine 2002).

The nano-TiC model seems attractive. While bulk TiC does not show any noticeable feature near $20.1\,\mu$m (Henning & Mutschke 2000), laboratory absorption spectra of TiC nanocrystals containing 27–125 atoms exhibit a distinct feature at $\sim 20.1\,\mu$m, closely resembling the astronomical $21\,\mu$m emission feature both in peak position, width, and in spectral details (von Helden et al. 2000). This model further gains its strength from the identification of presolar TiC grains (with radii $\sim 100\,\text{Å}$) in primitive meteorites as inclusions embedded in micrometer-sized presolar graphite grains (Bernatowicz et al. 1996).

Since Ti is a rare element, it is important to know whether the amount of TiC dust required to account for the observed $21\,\mu$m feature is a reasonable quantity. Since the optical properties of nano TiC in the ultraviolet (UV)/visible wavelength range are unknown, one has to rely on those of bulk TiC as a starting point. Such an attempt has recently been made for the post-AGB star HD 56126 by Hony et al. (2003). They found that to explain the observed $21\,\mu$m feature, the TiC model requires a much higher UV/visible absorptivity than that of bulk TiC (by a factor of $\gtrsim$20). However, we will demonstrate in this *Letter* how the TiC absorption integrated over a finite wavelength range places a lower limit on the TiC dust mass through the Kramers-Kronig dispersion relations. For HD 56126, this Kramers-Kronig lower limit exceeds the maximum available TiC mass by a factor of $\gtrsim$50, independent of the absolute value of the UV/visible absorptivity. Therefore, increasing the UV/visible absorptivity is unable to avoid the TiC abundance problem.

2. HD 56126: A Test Case

HD 56126, a bright (visual magnitude ~ 8.3) post-AGB star with a spectral type of F0-5I, is one of the four $21\,\mu$m sources originally discovered by Kwok et al. (1989). Mid-IR imaging of this object at $11.9\,\mu$m shows that its circumstellar dust is confined to an area of $1.2''$–$2.6''$ from the star (Hony et al. 2003). Detailed modeling of its dust IR spectral energy distribution suggested a $dn(r)/dr \sim 1/r$ dust spatial distribution at $r_{\rm min} \lesssim r \lesssim r_{\rm max}$, where r is the distance from the star, $r_{\rm min}$ and $r_{\rm max}$ are respectively the inner and outer edge of the HD 56126 dusty envelope (Hony et al. 2003). If TiC nanograins are indeed present in HD 56126 and follow the distribution of the bulk

(hydrogenated) amorphous carbon dust, the total power absorbed by the TiC dust would be[3]

$$E_{\rm abs}^{\rm tot}\,({\rm TiC}) = m_{\rm TiC}^{\rm tot}\frac{r_\star^2}{2}\frac{\ln\left(r_{\rm max}/r_{\rm min}\right)}{r_{\rm max}^2-r_{\rm min}^2}\int_{912\,\mathring{\rm A}}^{\infty}\kappa_{\rm abs}(a,\lambda)\,F_\lambda^\star d\lambda \quad , \tag{1}$$

where $m_{\rm TiC}^{\rm tot}$ is the total mass of the TiC nanoparticle component, $\kappa_{\rm abs}(a,\lambda)$ is the mass absorption coefficient ($\rm cm^2\,g^{-1}$) for nano TiC grains of size a at wavelength λ, $r_\star$ is the stellar radius, $F_\lambda^\star$ is the flux per unit wavelength ($\rm erg\,s^{-1}\,cm^{-2}\,\mu m^{-1}$) at the top of the illuminating star's atmosphere. In the nanometer size domain, TiC grains are in the Rayleigh limit and hence $\kappa_{\rm abs}(\lambda)$ is independent of size a in the wavelength range where the stellar radiation peaks. Following Hony et al. (2003), we will adopt a distance of $d \approx 2.4\,{\rm kpc}$ to the star (and therefore $r_{\rm min} \approx 4.3\times10^{16}\,{\rm cm}$, $r_{\rm max} \approx 9.3\times10^{16}\,{\rm cm}$), a stellar radius of $r_\star \approx 49.2\,r_\odot$ ($r_\odot$ is the solar radius), a stellar luminosity of $L_\star \approx 6054\,L_\odot$ ($L_\odot$ is the solar luminosity), and approximate the HD 56126 stellar radiation by the Kurucz (1979) model atmospheric spectrum with $T_{\rm eff} = 7250\,{\rm K}$ and $\log g = 1.0$.

The total power emitted in the $21\,\mu{\rm m}$ feature of HD 56126 was estimated to be $E_{\rm em}^{\rm tot}\,(21\,\mu{\rm m}) \approx 1.0\times10^{36}\,{\rm erg\,s^{-1}}$ (Hony et al. 2003). A *lower* limit on the total mass of the TiC dust required to account for the observed $21\,\mu{\rm m}$ feature can be obtained by assuming that all the energy absorbed by the TiC dust would be emitted solely in this feature:

$$m_{\rm TiC}^{\rm min} = E_{\rm em}^{\rm tot}\,(21\,\mu{\rm m})\,\frac{2}{r_\star^2}\frac{r_{\rm max}^2-r_{\rm min}^2}{\ln\left(r_{\rm max}/r_{\rm min}\right)}\Big/\int_{912\,\mathring{\rm A}}^{\infty}\kappa_{\rm abs}(\lambda,a)\,F_\lambda^\star d\lambda \quad . \tag{2}$$

Apparently, the required TiC dust mass $m_{\rm TiC}^{\rm min}$ is sensitive to the material's UV/visible absorptivity.

On the other hand, an *upper* limit on the total mass of the TiC dust which could be present in the circumstellar envelope around HD 56126 can be estimated from its photospheric Ti abundance $\rm Ti/H \approx 1.3\times10^{-8}$ (van Winckel & Reyniers 2000) and the envelope mass (including both gas and dust) $0.16 \lesssim m_{\rm env} \lesssim 0.44\,m_\odot$ (Hony et al. 2003): $m_{\rm TiC}^{\rm max} \approx 2.5\times10^{-7}\,m_\odot$.

3. Ultraviolet/Visible Absorption Properties of TiC Nanograins

Since the UV/visible absorption properties of nano TiC are unknown, we will first represent them by those of bulk TiC. Using Mie theory and the optical constants measured for bulk TiC samples (Koide et al. 1993), we calculate the UV/visible absorption efficiency $Q_{\rm abs}$ of spherical TiC nanograins. For illustration, we plot in Figure 1 the mass absorption coefficients ($\kappa_{\rm abs} = 3Q_{\rm abs}/\left[4a\rho_{\rm TiC}\right]$ where $\rho_{\rm TiC} \approx 4.92\,{\rm g\,cm^{-3}}$ is the TiC mass density) of TiC spheres of radii a=10 Å calculated from the optical constants of bulk TiC. Using these $\kappa_{\rm abs}$ values, we derive a lower limit

[3]The circumstellar envelope around HD 56126 is assumed to be optically thin. If there actually exists appreciable extinction (e.g., Hony et al. [2003] found an average visual extinction of $\sim$1.1 mag), the conclusion of this *Letter* would be strengthened since when exposed to an attenuated stellar radiation field, the TiC model would require more TiC dust to account for the same $21\,\mu{\rm m}$ feature strength.

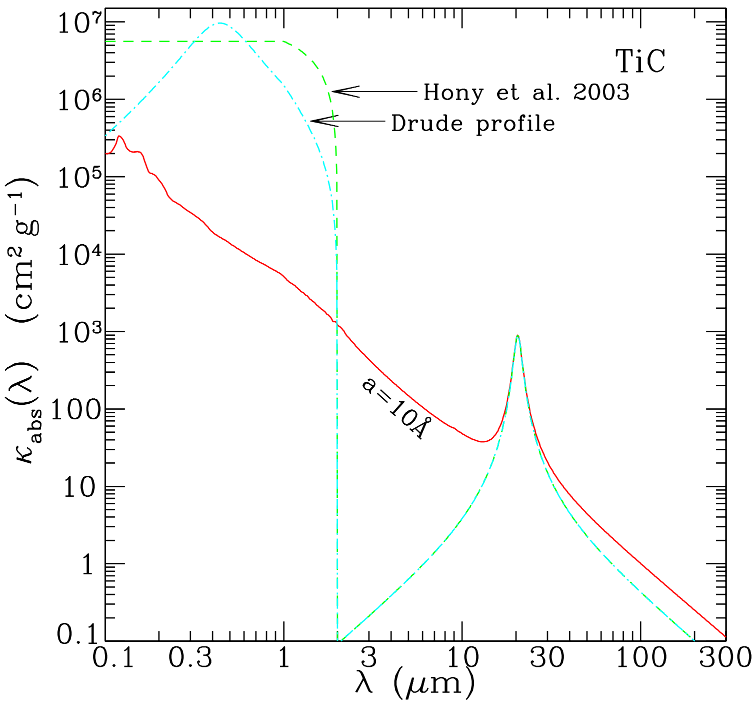

Fig. 1.— Mass absorption coefficients $\kappa_{\rm abs}(\lambda)$ of TiC nanograins of radii $a = 10\,$Å calculated (1) from the optical constants of bulk TiC (solid line), (2) from the Hony et al. (2003) hypothetical formula with $\kappa_{\rm abs}^{\rm UV} = 5.6 \times 10^6\,{\rm cm^2\,g^{-1}}$ (see Eq.[3]; dashed line), or (3) from a hypothetical Drude profile with $\kappa_{\rm abs}^{\rm UV} = 9.6 \times 10^6\,{\rm cm^2\,g^{-1}}$ (see §4; dot-dashed line). The IR part is the laboratory measured $21\,\mu$m spectrum of TiC nanocrystals (von Helden et al. 2000) approximated by a Lorentz profile (Chigai et al. 2003). It is apparent that the Hony et al. (2003) and Drude hypothetical absorption spectra greatly enhance the "ability" of TiC nanograins in absorbing the HD 56126 starlight.

of $m_{\rm TiC}^{\rm min} \approx 9.3 \times 10^{-5}\,m_{\odot}$ on the TiC dust mass from Eq.(2). Apparently, if nano TiC grains do not have a much higher UV/visible absorptivity than their bulk counterparts, they can not be the $21\,\mu$m feature carrier since the minimum required TiC dust mass is larger than the maximum available TiC mass ($m_{\rm TiC}^{\rm max} \approx 2.5 \times 10^{-7}\,m_{\odot}$; see §2) by over two orders of magnitude!

Hony et al. (2003) assumed a hypothetical absorption efficiency for TiC nanograins

$$\kappa_{\rm abs}(\lambda) = \begin{cases} \kappa_{\rm abs}^{\rm UV}\ , & 912\,\text{Å} \le \lambda \le 1\,\mu{\rm m}\ ; \\ \kappa_{\rm abs}^{\rm UV}\,(2-\lambda)\ , & 1\,\mu{\rm m} < \lambda \le 2\,\mu{\rm m}\ ; \\ 0\ , & \lambda > 2\,\mu{\rm m}\ ; \end{cases} \tag{3}$$

where $\kappa_{\rm abs}^{\rm UV}$ is the "constant level" UV/visible mass absorption coefficient. They concluded that the astronomical $21\,\mu$m feature could *only* be accounted for by the TiC model with a reasonable amount of TiC dust mass *if* nano TiC grains have an UV/visible absorption efficiency as high as $Q_{\rm abs}^{\rm UV} \approx 8$ where $Q_{\rm abs}^{\rm UV} = (4/3)\,a\rho_{\rm TiC}\kappa_{\rm abs}^{\rm UV}$.

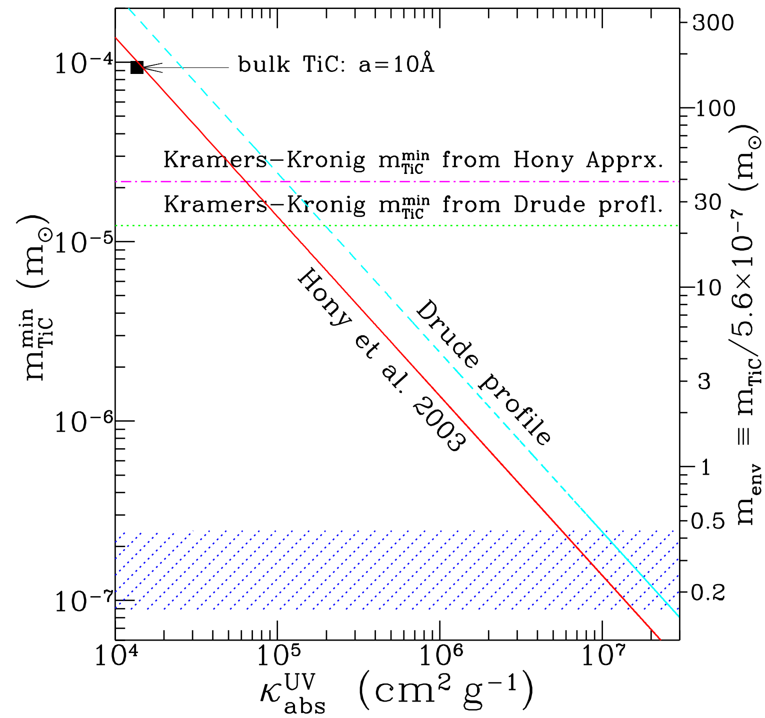

Fig. 2.— The TiC mass required to account for the observed 21 μm emission feature as a function of the UV/visible mass absorption coefficient $\kappa_{\rm abs}^{\rm UV}$ using the Hony et al. (2003) hypothetical formula (see Eq.[3]) or an optimized Drude profile (see §4). We also show the TiC mass derived from models using the optical constants of bulk TiC (filled square for grains of $a = 10\,$Å). The horizontal lines plot the Kramers-Kronig lower limits to the TiC mass inferred from the wavelength-integrated absorption cross sections based on the Hony et al. (2003) approximation (dot-dashed line) and the optimized Drude profile (dotted line) (both with $F = 1.5$; see §4 and Eq.[5]). The shaded area indicates reasonable values for the total available TiC dust mass (left axis) and the total envelope mass including both gas and dust (right axis).

In Figure 1 we also plot the Hony et al. (2003) hypothetical mass absorption coefficient with $\kappa_{\rm abs}^{\rm UV} = 5.6 \times 10^6\,{\rm cm^2\,g^{-1}}$. In comparison with the $\kappa_{\rm abs}(\lambda)$ values calculated from the optical constants of bulk TiC, the Hony et al. (2003) formula greatly enhances the ability of TiC dust in absorbing the HD 56126 stellar radiation which peaks at $\lambda \sim 0.45\,\mu$m. In Figure 2 we show the minimum TiC dust mass $m_{\rm TiC}^{\rm min}$ required to account for the observed 21 μm feature as a function of $\kappa_{\rm abs}^{\rm UV}$. It can be seen that if $\kappa_{\rm abs}^{\rm UV} \gtrsim 5.6 \times 10^6\,{\rm cm^2\,g^{-1}}$, the minimum required TiC dust mass could be smaller than the maximum available TiC mass, implying that the TiC model may be tenable.

4. Constraints from the Kramers-Kronig Relations

Let $C_{\rm ext}^{\rm tot}(\lambda)$ be the total extinction cross sections of TiC dust at wavelength λ, and $\int_0^\infty C_{\rm ext}^{\rm tot}(\lambda) d\lambda$ be the extinction integrated over the entire wavelength range from 0 to ∞. As shown by Purcell

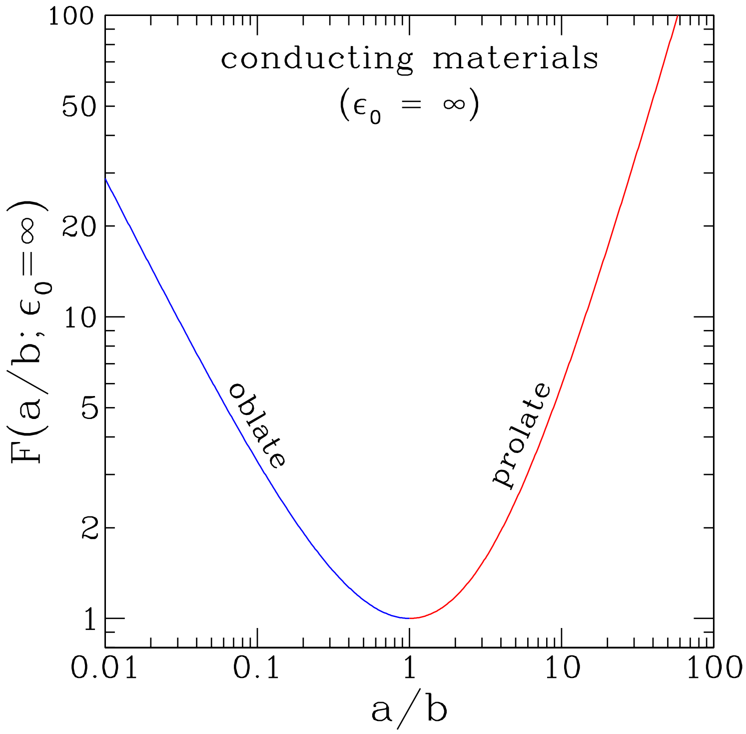

Fig. 3.— The $F(\epsilon_0;\text{shape})$ factor as a function of the axial ratio a/b for highly conducting spheroids (i.e., the static dielectric constant $\epsilon_0 \rightarrow \infty$). For modestly elongated ($a/b \lesssim 3$) or flattened ($b/a \lesssim 3$) grains, the F factor is not expected to significantly deviate from unity.

(1969), the Kramers-Kronig (KK) dispersion relations can be used to relate $\int_0^\infty C_{\rm ext}^{\rm tot}(\lambda)d\lambda$ to the total grain volume $V_{\rm tot}$ through

$$\int_0^\infty C_{\rm ext}^{\rm tot}(\lambda)d\lambda = 3\pi^2 V_{\rm tot} F\left(\epsilon_0;\text{shape}\right) \quad , \tag{4}$$

where F is the orientationally-averaged polarizability relative to the polarizability of an equal-volume conducting sphere (Purcell 1969; Draine 2003).

We can apply Eq.(4) to the HD 56126 circumstellar envelope to obtain a lower bound on the TiC dust mass $m_{\rm TiC}^{\rm KK}$, taking the envelope to be a vacuum sparsely populated by spheroidal TiC grains.[4] Since $C_{\rm ext}^{\rm tot} = \left(C_{\rm abs}^{\rm tot} + C_{\rm sca}^{\rm tot}\right) > C_{\rm abs}^{\rm tot} > 0$ (where $C_{\rm abs}^{\rm tot}$ and $C_{\rm sca}^{\rm tot}$ are the total absorption and scattering cross sections, respectively), the integration of $C_{\rm abs}^{\rm tot}$ over a finite wavelength range represents a lower limit to $\int_0^\infty C_{\rm ext}^{\rm tot}(\lambda)d\lambda$, and implies a lower limit to the volume of space which

[4] This is justified since the total volume of the TiC grains ($\sim 9.0\times10^{27}\,{\rm cm^3}$ for a total mass of $2.2\times10^{-5}\,m_\odot$) is negligible compared to the total volume of the dusty circumstellar envelope around HD 56126 ($\sim 3.1\times10^{51}\,{\rm cm^3}$). Apparently, the envelope also satisfies the prerequisite $|\epsilon-1| \ll 1$ for the KK relations to be applicable (where ϵ is not the dielectric constant of TiC, but of the envelope itself).

must be filled by TiC grains and hence a lower limit to the total TiC dust mass

$$
\begin{aligned}
m_{\rm TiC}^{\rm KK} &= \frac{\rho_{\rm TiC}}{3\pi^2 F\,(\epsilon_0;{\rm shape})} \int_{912\,\text{Å}}^{\infty} C_{\rm abs}^{\rm tot}(\lambda) d\lambda \\
&= \frac{m_{\rm TiC}^{\rm min}\,\rho_{\rm TiC}}{3\pi^2 F} \int_{912\,\text{Å}}^{\infty} \kappa_{\rm abs}(\lambda) d\lambda \\
&= \frac{2\rho_{\rm TiC} E_{\rm em}^{\rm tot}\,(21\,\mu{\rm m})\left(r_{\rm max}^2 - r_{\rm min}^2\right)}{3\pi^2 r_\star^2\,\ln\left(r_{\rm max}/r_{\rm min}\right)} \frac{\int_{912\,\text{Å}}^{\infty} \kappa_{\rm abs}(\lambda) d\lambda}{F \int_{912\,\text{Å}}^{\infty} \kappa_{\rm abs}(\lambda)\,F_\lambda^\star d\lambda}~. \qquad (5)
\end{aligned}
$$

The dimensionless factor F depends only upon the grain shape and the static (zero-frequency) dielectric constant ϵ_0 of the grain material (Purcell 1969; Draine 2003). Since TiC is a metallic material, we calculate the F factors expected for highly conducting materials (i.e., $\epsilon_0 \rightarrow \infty$) as a function of the axial ratio a/b (where a and b are the semiaxis along and perpendicular to the symmetry axis of the spheroid, respectively). As shown in Figure 3, F would not appreciably exceed unity unless the highly conducting grains are highly elongated (for prolates) or flattened (for oblates). If they are just modestly elongated ot flattened like interstellar grains ($a/b \sim 3$ [Greenberg & Li 1996] or $b/a \sim 2$ [Lee & Draine 1985]), we would expect $F \lesssim 1.5$. Therefore, it is reasonable to adopt $F = 1.5$ in the following discussions.

It is immediately seen in Eq.(5) that one cannot relax the TiC mass requirement just by increasing the UV/visible absorption level; instead, the Kramers-Kronig lower limit to the total TiC dust mass $m_{\rm TiC}^{\rm KK}$ is independent of the absolute level of $\kappa_{\rm abs}$. As discussed in §3, the nano-TiC model appears to be tenable if one adopts the Hony et al. (2003) $\kappa_{\rm abs}(\lambda)$ formula with $\kappa_{\rm abs}^{\rm UV} \gtrsim 5.6 \times 10^6\,{\rm cm^2\,g^{-1}}$. However, the KK relations (see Eq.[5]) results in a lower bound of $m_{\rm TiC}^{\rm KK} \approx 2.2 \times 10^{-5}\,m_\odot$ to the total TiC dust mass, exceeding the maximum available TiC mass of $m_{\rm TiC}^{\rm max} \approx 2.5 \times 10^{-7}\,m_\odot$ (see §2)[5] by a factor of ~ 90. Therefore, it appears that the nano-TiC model encounters great difficulty in meeting the TiC abundance constraint.[6]

One may argue that the Hony et al. (2003) formula (Eq.[3]) does not make economical use of the TiC absorption. A fine tuning on the spectral dependence of $\kappa_{\rm abs}(\lambda)$ might be able to enhance the grain's "ability" to absorb stellar radiation, resulting in an increase in $\int_{912\,\text{Å}}^{\infty} \kappa_{\rm abs}(\lambda)\,F_\lambda^\star d\lambda$ and a decrease in $m_{\rm TiC}^{\rm KK}$ (see Eq.[5]). We have tried models with a Drude profile-like UV/visible

[5] To be really generous, we can obtain an upper limit of $m_{\rm TiC}^{\rm max} \approx 6.1 \times 10^{-7}\,m_\odot$ by assuming that all Ti elements in HD 56126 (with a zero-age main-sequence mass of $\sim 1.1\,m_\odot$) have condensed in the form of TiC. The TiC model with $\kappa_{\rm abs}^{\rm UV} \gtrsim 2.3 \times 10^6\,{\rm cm^2\,g^{-1}}$ (see §3 and Eq.[3]) would then appear tenable since $m_{\rm TiC}^{\rm min} \lesssim m_{\rm TiC}^{\rm max}$. But the KK lower limit on the TiC mass $m_{\rm TiC}^{\rm KK} \approx 2.2 \times 10^{-5}\,m_\odot$ is far in excess of $m_{\rm TiC}^{\rm max}$ unless the TiC nanograins are extremely elongated ($a/b \gtrsim 25$) or flattened ($b/a \gtrsim 80$) so that $F \gtrsim 24$.

[6] In order for the TiC dust mass $m_{\rm TiC}^{\rm KK}$ derived from the KK relations not to exceed the maximum available TiC mass $m_{\rm TiC}^{\rm max}$, the TiC nanograins should be extremely elongated ($a/b \gtrsim 44$) for prolates or flattened ($b/a \gtrsim 220$) for oblates so that $F \gtrsim 59$. But it is hard to imagine how such extremely-shaped TiC nanograins could form and survive in circumstellar environments.

absorption spectrum[7] $\kappa_{\rm abs}(\lambda) = \kappa_{\rm abs}^{\rm UV}\,(\gamma\lambda)^2 \,/\, \left[\left(\lambda^2-\lambda_0^2\right)^2+(\gamma\lambda)^2\right]$ with $\lambda_0 = 0.44\,\mu$m and $\gamma = 0.35\,\mu$m (see Fig. 1) "*tailored*" to optimize the "ability" of TiC nanograins to absorb the HD 56126 stellar radiation. But it is found that models using this $\kappa_{\rm abs}$ functional form require a Kramers-Kronig lower limit of $m_{\rm TiC}^{\rm KK} \approx 1.2\times10^{-5}\,m_{\odot}$, still $\sim$50 times larger than the maximum available TiC mass.[8]

5. Discussion

In this *Letter* we have assumed that the TiC dust follows the spatial distribution of the bulk carbon dust (see §2). But this is not critical. Even if we assume that all the TiC dust accumulates at the inner edge of the envelope, to explain the observed $21\,\mu$m feature, one still needs $\sim$42% of the total TiC mass derived in §§3,4, since for the latter the average starlight intensity to which the dust is exposed is just $\sim$42% higher. Therefore, local density enhancement of TiC would not overcome the TiC abundance problem. High-resolution (FWHM $0.4''$) imaging at $20.8\,\mu$m revealed two bright blobs at $\sim 1''$ from the star, but their surface brightness is at most two times higher than the average (Kwok, Volk, & Hrivnak 2002), suggesting the insignificance of local density enhancement of the $21\,\mu$m feature carrier.

Von Helden etal. (2000) postulated that TiC nanograins could have formed during the extreme conditions (i.e., high density and high pressure) associated with the short, high mass-loss superwind phase where AGB stars lose the remaining stellar envelope, terminating their life on the AGB and starting the transition to the PN phase. However, Kwok et al. (2002) argued that there is no evidence that the $21\,\mu$m emission is created by a sudden ejection at the end of the AGB, implying that the necessary physical conditions required to form TiC in the ejecta of carbon-rich evolved stars may not be met.

In summary, although we are lack of experimental knowledge of the UV/visible absorption properties of nano TiC, a physical argument based on the Kramers-Kronig dispersion relations implies that the nano-TiC model requires too much Ti to reconcile with the observed photospheric Ti abundance.[9] Recently, the nano-TiC model was also challenged by Chigai et al. (2003), who found that the abundance ratio of Ti to Si needed to reproduce the observed flux ratios of the

---

[7]Spheroidal metallic nanograins are expected to have a Drude-profile like resonance if it is mainly due to free electrons (Bohren & Huffman 1983).

[8]A narrower $\kappa_{\rm abs}(\lambda)$ profile leads to a smaller $m_{\rm TiC}^{\rm KK}$, provided its peak is fixed at $\lambda_0 \approx 0.44\,\mu$m. However, even if we adopt an unphysical δ-function for $\kappa_{\rm abs}(\lambda)$, the corresponding KK lower limit $m_{\rm TiC}^{\rm KK} \approx 6.8\times10^{-6}\,m_{\odot}$ still exceeds $m_{\rm TiC}^{\rm max}$ by a factor of $\sim$27. We note that the grain surface scattering of electrons alone would result in a plasma resonance width of $\sim 0.1\,\mu$m for a 10 Å grain a typical Fermi velocity $v_F = 10^8\,{\rm cm\,s^{-1}}$ (see Li 2004).

[9]If these grains are coated by a mantle of graphite (see Chigai et al. 2003), the situation would be even worse since the large IR emissivity of graphite together with the fact that the increase in grain size may prohibit them from single-photon heating would jointly suppress emission in the $21\,\mu$m feature.

$11.3\,\mu$m SiC feature to the $21\,\mu$m TiC feature of post-AGB stars must be at least 5 times larger than the solar abundance ratio. Finally, we should note that laboratory absorption spectra of TiC nanoclusters also show prominent features at other wavelengths which are not seen in post-AGB stars (e.g. $Ti_{14}C_{13}$ also has a strong band at $\sim 16\,\mu$m; van Heijnsbergen et al. 1999).

I thank D. Arnett, A. Burrows, A.G.W. Cameron, S. Hony, D.S. Lauretta and K. Volk for helpful discussions/comments, T. Koide and D.W. Lynch for providing me with their optical constants of bulk TiC. I also thank the University of Arizona for the "Arizona Prize Postdoctoral Fellowship in Theoretical Astrophysics".

REFERENCES

Bernatowicz, T.J., Cowsik, R., Gibbons, P., Lodders, K., Fegley, B., Jr., Amari, S., & Lewis, R. 1996, ApJ, 472, 760

Bohren, C.F., & Huffman, D.R. 1983, Absorption and Scattering of Light by Small Particles (New York: Wiley)

Chigai, T., Yamamoto, T., Kaito, C., & Kimura, Y. 2003, ApJ, 587, 771

Draine, B.T. 2003, in The Cold Universe, ed. D. Pfenniger (Berlin: Springer-Verlag), in press

Greenberg, J.M., & Li, A. 1996, A&A, 309, 258

Henning, Th., & Mutschke, H. 2001, Spectrochim. Acta, 57, 815

Hony, S., Waters, L.B.F.M., & Tielens, A.G.G.M. 2001, A&A, 378, L41

Hony, S., Tielens, A.G.G.M., Waters, L.B.F.M., & de Koter, A. 2003, A&A, 402, 228

Koide, T., et al. 1993, Jpn. J. Appl. Phys., 32, 1130

Kwok, S., Volk, K., & Hrivnak, B.J. 1989, ApJ, 345, L51

Kwok, S., Volk, K., & Hrivnak, B.J. 1999, in IAU Symp. 191, Asymptotic Giant Branch Stars, ed. T. Le Bertre, A. Lébre, & C. Waelkens (San Francisco: ASP), 297

Kwok, S., Volk, K., & Hrivnak, B.J. 2002, ApJ, 573, 720

Lee, H.M., & Draine, B.T. 1985, ApJ, 290, 211

Li, A. 2004, in Astrophysics of Dust, ed. A.N. Witt, G.C. Clayton, & B.T. Draine (San Francisco: ASP), in press

Li, A., & Draine, B.T. 2002, ApJ, 564, 803

Purcell, E.M. 1969, ApJ, 158, 433

Smith, T.L., & Witt, A.N. 2002, ApJ, 565, 304

Speck, A.K, & Hofmeister, A.M. 2003, ApJ, in press

van Heijnsbergen, D., et al. 1999, Phys. Rev. Lett., 83, 4983

van Winckel, H., & Reyniers, M. 2000, A&A, 354, 135

Volk, K., Kwok, S., & Hrivnak, B.J. 1999, ApJ, 516, L99

von Helden, G., et al. 2000, Science, 288, 313

This preprint was prepared with the AAS LaTeX macros v5.0.